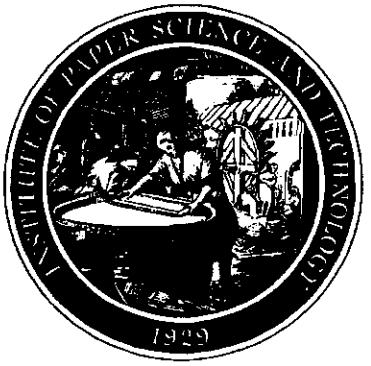

Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 888

The Influence of Humidity Cycling Parameters on the Moisture Accelerated Creep of Polymeric Fibers

C.C. Habeger, D.W. Coffin, and B. Hojjatie

January 2001

Submitted to
Journal of Polymer Science
Part B: Polymer Physics

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929 as the Institute of Paper Chemistry, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 51 member companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide a multidisciplinary graduate education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to provide the information, expertise, and interactive learning that enables customers to improve job knowledge and business performance;
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

The Influence of Humidity Cycling Parameters on the Moisture Accelerated Creep of Polymeric Fibers

C. C. Habeger, D. W. Coffin, and B. Hojjatie

Institute of Paper Science and Technology, Atlanta, Georgia

Synopsis

Accelerated creep is a curious and poorly understood transient moisture effect. The creep rates of most hydrophilic materials increase greatly with moisture content. However, when these same materials are subjected to creep loads in cyclic humidity environments, they often exhibit much higher creep rates than in a constantly humid state. This is called accelerated creep. Previous experimenters report that accelerated creep is less likely to occur in polymeric fibers. We demonstrate experimentally that this was due only to their choice of humidity cycling parameters. New results are contributed for Kevlar, lyocell, Nylon 6,6, and ramie fibers. Other paper scientists have argued that the absence of accelerated creep in single fibers supports a explanation based on fiber network effects for accelerated creep in paper. We argue here that accelerated creep is a more general phenomena consistent with the sorption-induced stress-gradient explanations.

Introduction

Transient moisture effects, a.k.a. mechano-sorptive effects, are anomalous, sorption-induced influences on the mechanical properties of materials. Accelerated creep is a prime example of a transient effect. Hydrophilic materials almost always exhibit increases in creep compliance with increasing moisture content. Nonetheless, they often experience much greater creep in cyclic humidity conditions than in a constant environment at the high humidity extreme. The mechanisms of accelerated creep are highly contentious topics, and there is no widely accepted explanation. Extra creep under varying humidity conditions has been attributed to increased molecular mobility during moisture transport (1-4), increased molecular mobility during moisture change (5-9), sorption-induced physical aging (10), material-specific interfiber mechanisms (11-14), thermodynamic ratcheting actions (15), and sorption-induced stress gradients (16-18).

Many materials are purported to exhibit accelerated creep. These include concrete (16), wood (19-21), paper (22,23), polyurethane foams (24), Kevlar-reinforced composites (25), and Kevlar fibers (9,25,26). Single wood fibers are observed not to experience accelerated creep (27-29), whereas paper sheets made from identical fibers and tested in the same apparatus do show a great deal of extra creep under the same cyclic humidity conditions (29). Likewise, cellophane, a regenerated cellulose film, does undergo accelerated creep (18); however, rayon, a regenerated cellulose fiber, is reported to be immune from the effect (30). Also, negative results (26) have been published for poly(methyl methacrylate) fibers. On the other hand, spun cellulose acetate butyrate

fibers show accelerated creep (26). Nylon 6,6 is classified as a non participant in both its fibrous (25,30) and injection molded (32) forms. With the exception of Nylon 6,6, all reports of the nonoccurrence of accelerated creep in hydrophilic materials stem from single fiber experiments. Conclusions regarding the behavior of single fibers are mixed; some fiber types submit to accelerated creep, whereas others seem to resist.

The purpose of this paper is to clarify the seeming disparity between single-fiber and larger-sample tendencies for accelerated creep. We are vocal adherents of the sorption-induced stress gradient explanation. We argue from this theoretical perspective that the widespread lack of observance of single-fiber accelerated creep is due to an experimental detail rather than a fundamental difference in material behavior. In order for "moisture-gradient-driven" accelerated creep to occur, the time parameters of the humidity cycling must be matched to the sorption time of the sample. We argue that this match was not fortuitous in some of the previous single-fiber experiments. We report experiments demonstrating that fiber accelerated creep is sensitive to cycling time parameters and sorption times and that accelerated creep can be pronounced when the cycling is just right. Under favorable conditions, we observe accelerated creep even in Nylon 6,6 fibers. Nonetheless, we concur that Nylon 6,6 is unusually resistant to accelerated creep. We speculate on reasons for this but we provide no conclusive arguments. Our opinion, bolstered by the new experiments and an appeal to the sorption-induced stress gradient mechanism, is that accelerated creep is a more general phenomenon than commonly believed. Unless there is something very unusual in the sorption or mechanical properties of a hydrophilic material, with proper humidity cycling, it should exhibit accelerated creep.

Sorption-Induced Stress-Gradient Explanation:

We have published (18) our interpretation of the sorption-induced stress-gradient mechanism for accelerated creep. The following is a short synopsis concentrating on the time-scale issues that motivated the experiments reported below. The crux of the argument is that cyclic sorption leads to localized cyclic loading and that materials creep more under cyclic load than at a constant, average load. Imagine a sample undergoing tensile creep. A uniform stress field is established across the sample. The chamber humidity suddenly decreases. The sample starts to dry from the outside in. The outer regions respond by shrinking and increasing their elastic moduli. This transfers tensile load from the interior to the exterior. As desorption progresses the stresses are further redistributed across the sample. If no further environmental changes are imposed, the sample approaches moisture equilibrium and the stress gradients relax away. Each portion of the sample has experienced a stress disturbance: the exterior had a temporary stress increase, whereas the interior stress dropped below the average for a while. Now, if the humidity returns to its original level, the stress gradient history reverses. This time, the inside gets the stress spike. Through a continuation of these processes, moisture cycling causes out-of-phase, localized load cycling. The additional creep during the high-load excursions can more than make up for the reduced creep during below average load periods, and the total creep is greater upon cyclic loading than at a constant, average

load. If these localized, high-load creep surges overcompensate for the reduced overall creep rate at the lower average moisture content, the sample will creep more under cyclic humidity than at uniform high moisture content. We call this moisture-gradient-driven accelerated creep (18). Sorption can also cause stress gradients in a material that is heterogeneous in its response to moisture: heterogeneity-driven accelerated creep. Heterogeneity may play a role in the accelerated creep of paper (33), but in this study single fibers are the concern, and the moisture-gradient-driven action is most probably dominant.

The moisture-gradient-driven mechanism is potent only if the stress spikes are large and persist for a major portion of the total creep time. For simplicity, consider a humidity cycling regime as depicted in Figure 1. If the sorption time is small compared to the ramp time, the sample moisture profile will be nearly flat during sorption. No significant stress gradients will arise, and there will be no accelerated creep. So the humidity must be changed rapidly. Also, the cycle time must be tuned to the sorption time. If the cycle time is very long, there will be relatively few sorption events, and stress gradients will persist for only a small portion of the creep time. On the other hand, if the cycle time is less than the sorption time, the moisture gradients will develop only at the surface of the sample, and the interior will not receive the necessary load cycling. A large moisture-gradient-driven accelerated creep result requires that the ramp time be less than the sorption time and the sorption time be of the order of, but less than, the cycle time.

To argue that the mechanism is sufficient to account for the accelerated creep observed in paper, we developed a simple mathematical model (18). It can also be used to elucidate the qualitative points made above. The model treats a specimen as two mechanical elements sharing load in parallel. Both elements are given moisture-dependent mechanical properties (creep, elastic modulus, and hygroexpansion) similar to those observed in the material of interest. Upon sorption, one element (the outside element) changes moisture content linearly over a time period equal to one half the sorption time plus the ramp time. The inside element's moisture content changes at the same rate, but delayed by one half the sorption time. The sorption delay causes load shifting between the elements.

With an appropriate creep constitutive equation and the right relationships between sorption, cycle, and ramp times, the model reproduces accelerated creep. Figure 2 documents a simulation using paper properties. Here, the environmental and sorption time parameters were selected to give near-optimal accelerated creep: ramp time equals five minutes, sorption time equals twenty minutes, and cycle time equals two hours. The sample is held under load in the wet state for 2.5 hours, at which time the moisture cycling begins. The top graph contrasts the creep behavior for samples in the cyclic moisture and always wet (dashed line) states. The bottom graph documents the load cycling between the elements. The relative load on the outside (first-to-sorb) element is plotted versus cycle number. At the beginning of the first drying cycle the outside element experiences a load spike. It initially creeps rapidly, and by the time the inside

element is also dry the load has shifted inside. Under the uniformly dry conditions, the more heavily loaded element creeps faster, and the load distribution relaxes back towards an even divide. Upon rewetting the action reverses: the inside element gets the first load spike, the load shifts to outside as the inside moisture content catches up, and the load difference relaxes away under the all-wet condition. Notice that the time parameters were adjusted so that the load was well mismatched over the entire moisture cycle. As displayed in the top graph, the simulated accelerated creep is considerable.

Figure 3 documents another run with only one adjustment: the sorption time was reduced from 20 minutes to 2 minutes. This exercise is intended to demonstrate what might happen if a fiber sample was tested under conditions that generated accelerated creep in a larger test piece. Now (bottom graph), the load mismatch is greatly reduced in magnitude and duration. Due to the lesser creep at low moisture content, the sample creeps more slowly under cyclic humidity than at constant high humidity. Accelerated creep disappears. The other extreme is represented by Figure 4. This time, sorption time was increased to 200 minutes. For this sample, the cycling is too fast to allow full sorption and desorption. Hygroexpansion is attenuated. The moisture gradients are small, and there is no accelerated creep. Accelerated creep could also be foiled by extending the cycle time. The load distribution would have time to relax between humidity changes, and the extra creep from the relatively rare sorption events would not overcome the lesser average creep rate at the lower average moisture content.

So far, we have tacitly assumed that air at the specimen surface had the same relative humidity as the bulk of the chamber. During sorption, however, there is a convection boundary layer. Part of the water chemical potential difference between the bulk of the chamber and the center of the sample is across this layer. If the convection contributes a large portion of the resistance to moisture transport, moisture gradients across the sample will be attenuated, and accelerated creep will not happen. This occurs when moisture diffuses rapidly through the material, the sample cross section is small, and the chamber is stagnant. The small cross section of the samples used in single-fiber accelerated creep testing mitigates against the phenomenon for two reasons: it is likely the sorption time will be much less than ramp time and cycle time, and the convection boundary layer plays a greater role in moisture transport. Below, we argue that this is the reason that accelerated creep is often not observed in single-fiber experiments.

Experiment:

Two different instruments were used for the creep measurements. The Kevlar experiments were done in a chamber borrowed from Dave Dillard of Virginia Polytechnic Institute and State University. It is described in detail elsewhere (34). Briefly, a vertical glass tube with wet and dry air ports acts as an environmental chamber. A test fiber is suspended down the center of the tube. Its bottom end is glued to the core of an LVDT. The core passes through a small hole in the bottom of the chamber into an externally mounted LVDT coil. Small extra weights can be suspended from the core. A

computer controls the air ports and monitors the LVDT, the chamber temperature, and relative humidity.

The other fibers had greater ratios of hygroexpansion-to-creep strain, and it was important to have better control over the humidity in order to get repeatable creep results. Therefore, we modified a creep tester (18) designed for paper strip samples so that it could accommodate fibers. The paper tester has a chamber with active humidity control under computer direction. Otherwise, the two testers are functionally equivalent. For all tests, the samples were preconditioned in an unloaded state at the initial humidity for at least 16 hours before a creep load was applied.

Kevlar Fibers:

Kevlar is one of the few hydrophilic materials that is thus far reported to undergo accelerated creep in fiber form. Wang and Dillard et al. (9,25,26) report positive results for 1.5-denier Kevlar 29, Kevlar 49, and Kevlar 149 fibers at 60 °C. We recently confirmed their observations with room temperature experiments on 1.5-denier Kevlar 29 fibers with a 0.056-N load (see Figure 5). They cycled humidity at two-hour intervals between 95 and 5% RH, whereas we went between 90 and 10% RH at one-hour intervals. Kevlar is slow sorbing compared to other hydrophilic fibers: sorption times for Kevlar fibers of this diameter are in the 10 to 20-minute range (35). In both cases, ramp times were a few minutes; therefore, the sorption, cycle, and ramp times were well tuned for occurrences of moisture-gradient-driven accelerated creep.

Spun aromatic polyamide Kevlar fibers have unusually high axial moduli and tenacities. They are highly crystalline, and the crystalline chains are preferentially oriented toward the fiber axis. As load increases, the crystalline chains become more oriented to the fiber axis. This results in an increase of tangent modulus (36,37) and a decrease in creep compliance (38). The moisture-gradient-driven accelerated creep explanation relies on a special feature of the material creep constitutive equation: creep is amplified by load cycling. At first, it seems that Kevlar, with its insensitivity of creep rate to load, will not have the requisite behavior. However, creep at constant load and cyclic-load creep are very different experiments. Under steady load, creep compliance generally decreases with time. At the time of high load application in load cycling, the material has not lost creep compliance from longtime creep at high load. It does not necessarily follow that loss in creep compliance with load rules out cyclic-load creep amplification. Direct experiments are needed.

A room-temperature, 90 % RH, cyclic-load creep curve of a 1.5-denier Kevlar 29 fiber is presented as Figure 6. A tensile load of 0.0559 N was applied for 2 hours. Then the load was cycled between 0.0304 and 0.0813 N at 1-h intervals. After three cycles the load was returned to its original value and the creep experiment continued. The average load during the cycling period was equal to the constant creep load. Kevlar's constant-load creep strain, as plotted in Figure 6, is linear with logarithm of time (25,38). By extension of the constant-load line, notice that load cycling has greatly increased the

average creep rate. The total creep deformation during the load cycling period was about six times greater than it would have been if the load had remained steady. After load cycling, the constant-load creep rate was greatly reduced, but it would take a very long time before the two curves would meet. Even though creep rate is relatively independent of load in Kevlar, load cycling produces a large injection of extra creep strain. These Kevlar fiber experiments have the required characteristics for moisture-gradient-driven accelerated creep: proper moisture cycling and proper creep constitutive behavior.

Cellulose

The lifetimes of corrugated paperboard boxes are greatly reduced as a result of diurnal temperature and humidity cycling in warehouses. These boxes must be overbuilt to survive cyclic environments; thus it is exceedingly important to understand and remedy paperboard accelerated creep. It has long been well established that paper is very susceptible to accelerated creep (39). Recently, however, experimenters (27-29) have reported that wood fibers do not show accelerated creep when tested individually. Our rivals, those who explain paper accelerated creep in terms of interfiber interactions, believe that these results enforce their position (39,40). If fibers alone do not do it, they argue, it must be in the structure. Our goal is to demonstrate that accelerated creep is inherent in cellulose.

We begin with a closer look at Sedlachek's single-fiber results (27,28). The fibers were extracted holocellulose loblolly pine fibers. The cell wall thickness was measured at about 9 μm, and the fibers sorbed very rapidly. Fiber specimens were weighed in a chamber at 1-minute intervals during relative humidity cycling. Moisture content appeared to reach equilibrium almost instantly, limiting the sorption time to considerably less than 1 minute. Figure 7 is a reproduction of typical cyclic humidity creep results. Strain versus time plots are presented for 90% RH, 50% RH and 10-minute cycling between 90 and 50 % RH. The chamber humidity ramp time was estimated at 15 seconds. So the ramp time was at least as great as the sorption time, and the cycle time was much greater than the sorption time. These conditions are not conducive for observation of strong moisture-gradient-driven accelerated creep. It is no wonder that the order of fivefold increases in creep rates observed in paper samples under the same humidity cycling conditions were not repeated here.

Nonetheless, something is happening. The cyclic humidity creep is roughly the same as the wet creep; it is clearly above the average of dry and wet creep. Arbitrarily, the threshold for classification of accelerated creep is set high. A material is deemed to experience accelerated creep only if its creep under cyclic humidity is much greater than that in the wet state. One should not infer that wood fiber creep is not facilitated by cyclic humidity conditions merely because its creep rate does not clear this high-bar definition. The Sedlachek wood fiber experiments are on the verge of showing accelerated creep. If the moisture-gradient-driven picture is correct, they could be pushed along by increasing sorption time or by decreasing ramp time or cycle time.

Giving further solace to paper-structure advocates, rayon fibers (solvent-spun regenerated cellulose fibers) are also reported not to experience accelerated creep (30). Wood fibers are a conglomerate of cellulose, hemicellulose, and lignin. The cellulose is more crystalline in the wood fibers, but cellulose is the basic load-carrying material in both fiber types, and the two should exhibit the same general mechanical phenomena. In these rayon fiber experiments, the humidity cycle time was 40 minutes and the chamber had a 10-second ramp time. However, the fibers were thin (diameter about 12 μm, denier about 1) and thereby fast-sorbing. Again, the non classification was a result of the high threshold. The cyclic humidity creep was greater than the low-high humidity average creep and nearly equal to the high humidity creep. Because of their rapid sorption and the larger influence of the convention boundary layer in moisture transport, we believe it will be difficult to observe strong accelerated creep in experiments with thin cellulose fiber experiments. On the other hand, moderate levels of accelerated creep have been reported for cellulose acetate butyrate fibers (26) under a 4-hour humidity cycle time. We attribute this to the larger diameter of the CAB fibers (about 160 μm).

To investigate the influence of sorption time on cellulose accelerated creep, we decided to experiment with larger fibers. This necessarily meant working with synthetic fibers. Like rayon, lyocell fibers are solvent-spun cellulose fibers. They differ somewhat in structure. Lyocell fibers have longer crystallites and shorter, better-oriented amorphous regions. They are stiffer, stronger, and less moisture absorbent. If anything, they should be less prone to sorption amplified creep. Thanks to the generosity of Jason Yorke of Acordis, we obtained specially spun lyocell fibers with a range of unusually large deniers. As documented by Figure 8, we found through cyclic-load testing that these fibers had the right creep constitutive behavior to experience moisture-gradient driven accelerated creep. A 3-cm long, 71-denier lyocell fiber (draw ratio: 14.3) was strained in the multi specimen creep tester for 2 hours with a 38-gram load. Then it was load cycled at one hour intervals between 55 and 21 g. At the end, the creep test was continued with the 38-g load. This is different from the Kevlar response (Figure 6) in that creep strain is larger in relation to the elastic strain, and the high-load creep rate, especially in the first cycle, is more pronounced. Nevertheless, the conclusion is the same: cyclic loads cause much more creep than static loads at the same average load.

To emphasize the importance of cycle time, we modified the standard humidity cycling regime. Samples were treated to humidity cycling at progressively greater cycle times keeping the ramp times constant (1 minute wet-to-dry, 5 minutes dry-to-wet). The humidity cycling started at 10 minutes. After about 10 cycles, it was switched to 30 minutes. Later still, it was increased to two hours, and at the very end there were two 6-hour cycles. Figure 9 gives the creep strain and humidity time profile for an 11-denier lyocell fiber (draw ratio: 5.8) with a 16-g load. Results for a larger, 177-denier fiber of the same draw ratio with a 2.0-N load follow as Figure 10. Notice that the degree of accelerated creep depends on the cycle time and that the between-cycle-time comparisons depend on the fiber diameter. The faster sorbing, smaller fiber experiences its greatest accelerated creep at highest cycling rate. Sorption is always able to keep up with the cycling, and the portion of time under sorption decreases with cycle time. The larger-

diameter fiber has a maximum in accelerated creep at the intermediate cycle time. Its low cyclic strain amplitude under rapid cycling is evidence that it sorbs too slowly to approach moisture equilibrium during the 10-minutes cycling phases. In summary, lyocell fibers exhibit accelerated creep only if humidity cycling is tuned properly, and the optimum cycling parameters depend on fiber thickness.

By tuning the humidity cycling to the sorption time, we forced lyocell fibers into accelerated creep. Since these are synthetic fibers, there still could be some doubt as to the likelihood for wood fiber accelerated creep under proper cycling conditions. Wood fibers generally sorb too rapidly for proper cycle timing in our humidity chamber. All the same, we felt compelled to demonstrate the phenomenon on a natural cellulose fiber. Bast fibers from ramie were the best specimens available for this purpose. They are thick enough to sorb relatively slowly and long enough to be measured accurately in our creep apparatus. Humidity cyclic creep results for a 30-μm diameter, 2-cm long ramie bast fiber are presented in Figure 11. During the rapid cycling phase, it clearly exhibits accelerated creep.

Also, in support of the fiber-structure explanations, it is claimed that, unlike paper, regenerated cellulose films (cellophane) do not experience accelerated creep (13). We attribute this conclusion to an unfortunate selection of humidity cycling parameters in the cited cellophane test. The humidity was ramped up linearly over a 1-hour period. Then, it was ramped down over the next hour and left in the dry state for a third hour before embarking on the second humidification step. The ramp time was definitely longer than the sorption time, and the humidity cycling was slanted towards the dry side. From the moisture-gradient-driven perspective, it is no surprise that creep under these conditions was much less than it was in the humid state. When humidity was evenly cycled at 1-hour intervals and the ramp time was shortened to a few minutes, we found that cellophane did experience accelerated creep (18).

Nylon 6,6

Nylon 6,6 is hydrophilic polymer that undergoes a large amount of hygroexpansion; it appears to be an excellent candidate for accelerated creep. Hunt and Darlington (32) made cyclic humidity creep experiments on 1-mm-thick tensile coupons. They report (their Figure 5) no anomalous effects. However, we note that cycle time (336 hrs) was much shorter than the sorption time (about 2000 hrs). This puts the moisture-gradient-driven mechanism in the realm of our Figure 4, and we do not expect to see accelerated creep. Nonoccurrence in Nylon 6,6 fibers is reported from two sources. Salmen and Fellers (31) find that cyclic creep is about equal to high humidity creep when 30 fiber bundles of 17-denier fibers are treated to humidity cycles of about 6 hours. The fiber bundles clearly sorb much faster than the cycle time; therefore, we assert that the cycle parameters were not properly optimized to observe accelerated creep. The same is true for the Wang et al. experiments (25). It is clear from the strain curves (Figure 8, (25)) that the sorption time is much less than the 10^4-s cycle time.

We also made experiments on Nylon 6,6 using larger fibers and cycling humidity faster. Load cycling results for a 40-denier fiber are presented as Figure 12. Since the after-cycling creep strain is well above the projected constant load level, we conclude that the creep behavior of Nylon 6,6 fibers has the proper load dependence to participate in moisture-gradient-driven accelerated creep. Figure 13 documents 0.5-h and 2-h humidity cycling for a 15-denier fiber, whereas Figure 14 has results for a 40-denier fiber with 10-m, 0.5-h, and 2-h cycling. Notice there is a small but significant degree of accelerated creep. Due to differences in sorption time, the 0.5 h cycle creep rate is greater than at 2 h for the 15 denier (Figure 13) but about the same for the 40-denier fiber (Figure 14). Over a set of five tests (not graphed here), the log. time slope of the creep strain curve is about 50% greater under cyclic humidity than at high humidity for 15-denier fibers and about 25% greater for 40-denier fibers.

We did detect accelerated creep in Nylon 6,6 fibers; however, the magnitudes were well below those of experiments on any of the other hydrophilic materials with properly tuned cycling. The reason does not appear to be in the creep constitutive equation; however, there are other issues that influence moisture-gradient-driven accelerated creep (18). In tensile creep, the sorption-induced overload is on the drier portion of the material. Accelerated creep should be greater in materials with large dependence of modulus on moisture content and smaller dependence of creep rate on moisture content. Higher dry modulus causes greater tensile stress gradients, whereas lesser moisture creep dependence leads relatively greater creep in highly stressed dry regions. Also, the form of the moisture dependence of diffusivity could play a role. Materials that diffuse moisture as a front should establish larger stress gradients during sorption. We have not made a comparative study of Nylon 6,6 in terms of these properties, but it is a possibility for future work.

Conclusions

We have experimentally demonstrated that accelerated creep is a more general phenomenon than is normally accepted. Previous efforts to detect accelerated creep in polymeric fibers failed due to improper choices of humidity cycling times. We have argued the observation of fiber accelerated creep under proper cycling is consistent with the moisture-gradient-driven stress concentration explanation. The relatively small degree of accelerated creep in Nylon 6,6 remains unexplained.

Acknowledgements

We gratefully acknowledge the Member Companies of the Institute of Paper Science and Technology for funding this work. We are indebted to Jason Yorke of Acordis Tencel Non Woven Group in Derby, UK, for the custom manufacture of the high-denier lyocell fibers. Hiroki Nanko of IPST recommended the testing of ramie fibers and supplied the samples.

References

1. Ericksson, L.; Noren, B. Holz als Roz- und Werkstoff 1965, 23(5), 201-209.
2. Gibson, E. J. Nature 1965, 206(4980), 213-215.
3. Bethe, E. Holz als Roz- und Werkstoff 1969, 27(8), 291-303.
4. Bazant, Z. P. Wood Sci Technol 1985, 19, 159-177.
5. Ranta Maunus, A. Wood Sci Technol, 1975, 9, 189-205.
6. Hunt, D. G. J Mater Sci 1986, 21, 2088-2096.
7. Van der Put, T. A. C. M., Thesis Delft University Press 1989.
8. Hanhijarvi, A. Wood Sci Technol 1995, 29, 191-195.
9. Wang, J. Z.; Dillard, D. A.; Ward, T. C. J Polym Sci Part B Polym Phys 1992, 30, 1391-1400.
10. Padanyi, Z. V. Proc. 1991 International Paper Physics Conference, Kona Hawaii, 1991, pp 397-411.
11. Soremark, C.; Fellers, C. N. J Pulp Paper Sci 1993, 19(1), J19-J26.
12. Soremark, C.; Fellers, C. N.; Hendriksson, L. In Trans. 10th Fund. Res. Sym. at Oxford, 1993, pp 547-574.
13. Haslach, H. W. Tappi 1994, 77(10), 179-186.
14. Haslach, H. W. Mechanics of Time-Dependent Materials 2000, 4: 169-210.
15. Caulfield, D. F. Proc. Moisture-Induced Behavior of Paper and Board Conference Stockholm, 1994, pp 89-103.
16. Pickett, G. J. J Amer. Concrete Inst. 1942, 13(4), 333-355.
17. Selway, J. W.; Kirkpatrick, J. Proceedings: Cyclic Humidity Effects on Paperboard Packaging, FPL Madison, WI, 1992, pp 31-47.
18. Habeger, C. C.; Coffin, D.W. J of Pulp and Paper Sci 2000, 26(4), 145-157.
19. Armstrong, L. D.; Kingston, R. S. T. Nature 1960, 185 (4716), 862-863.
20. Armstrong, L. D.; Christensen, G. N. Nature 1961, 191 (4791), 869-870.
21. Armstrong, L. D.; Kingston, R. S. T. Aust J Appl Sci 1962, 13(4), 257-276.
22. Byrd, V. L. Tappi 1972, 55(2), 247-252 .
23. Byrd, V. L. Tappi 1972, 55(11), 1612-1613.
24. Dounis, D. V.; Moreland, J. C.; Wilkes, G. L.; Dillard, D. A.; Turner, R. B. J Appl Polym Sci 1993, 50, 293-301.
25. Wang, J. Z.; Dillard, D. A.; Wolcott, M. P.; Kamke, F. A.; Wilkes, G. L. J Comp Mater 1990, 24, 994-1009.
26. Wang, J. Z.; Vipul, D.; Glasser, W.; Dillard, D. A. In High Temperature and Environmental Effects on Polymeric Composites ASTM STP 1174, C. E. Harris and T. S. Gates Eds. Amer. Soc. for Testing and Mater., Philadelphia: 1993, pp 186-200.
27. Sedlachek, K. M. Thesis, Institute of Paper Science and Technology, 1995.
28. Sedlachek, K. M. Ellis, R. L. Proc. Conf. Moisture-Induced Creep Behavior of Paper and Board, STFI Stockholm, 1994, pp 29-49.
29. Coffin, D. W.; Boese, S. B. Proc. Moisture and Creep Effects on Paper, Board and Containers, PAPRO Rotorua, N.Z, 1997, pp 39-52.
30. Jackson, T.; Parker, I. Proc. Moisture and Creep Effects on Paper, Board and Containers, PAPRO Rotorua, N.Z., 1997, pp 53-67.
31. Salmen, L.; Fellers, C. N. Nordic Pulp and Paper Res J 1996, 11(30), 186-191.

32. Hunt, D. G.; Darlington, M. W. Polymer 1980, 21: 502-508.
33. Coffin, D. W.; Habeger, C. C. Tappi March 2001
34. Wang, J.Z.; Dillard, D.A. Experimental Techniques 1991, 15(5), 47-49.
35. Fukuda, M.; Kawai, H. Textile Res J 1993, 64(3), 185-193.
36. Northolt, M. G., van Aartsen, J.J. J Polymer Sci: Polymer Symposium 1977, 58, 283-296.
37. Northolt, M. G. Polymer 1980, 21, 1199-1204.
38. Ericksen, R. H. Polymer 1985, 26, 733-746.
39. Haslach, H. W. In Vol. 1 Handbook of Physical Testing of Paper, Mark, R. E., Ed.; marcel dekker: New York, 2001; Chapter 4, pp 173-232.
40. Haslach, H. W.; Wu, X., Mechanics of Cellulosic Materials, ASME, 1992, AMD-Vol. 145/MD-Vol 36, 39-47.

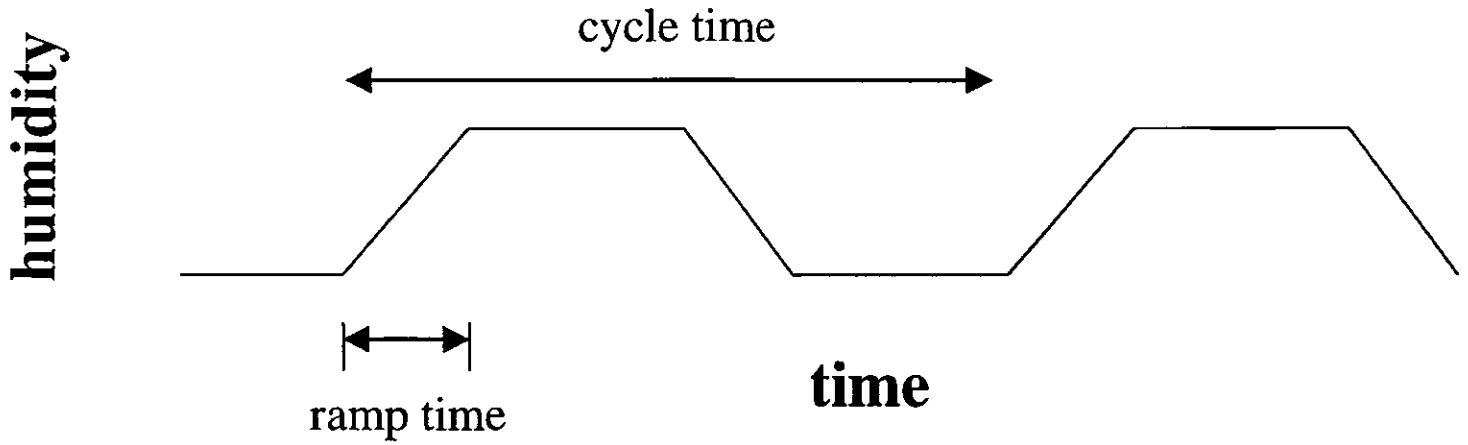

Figure 1
Humidity cycling terminology

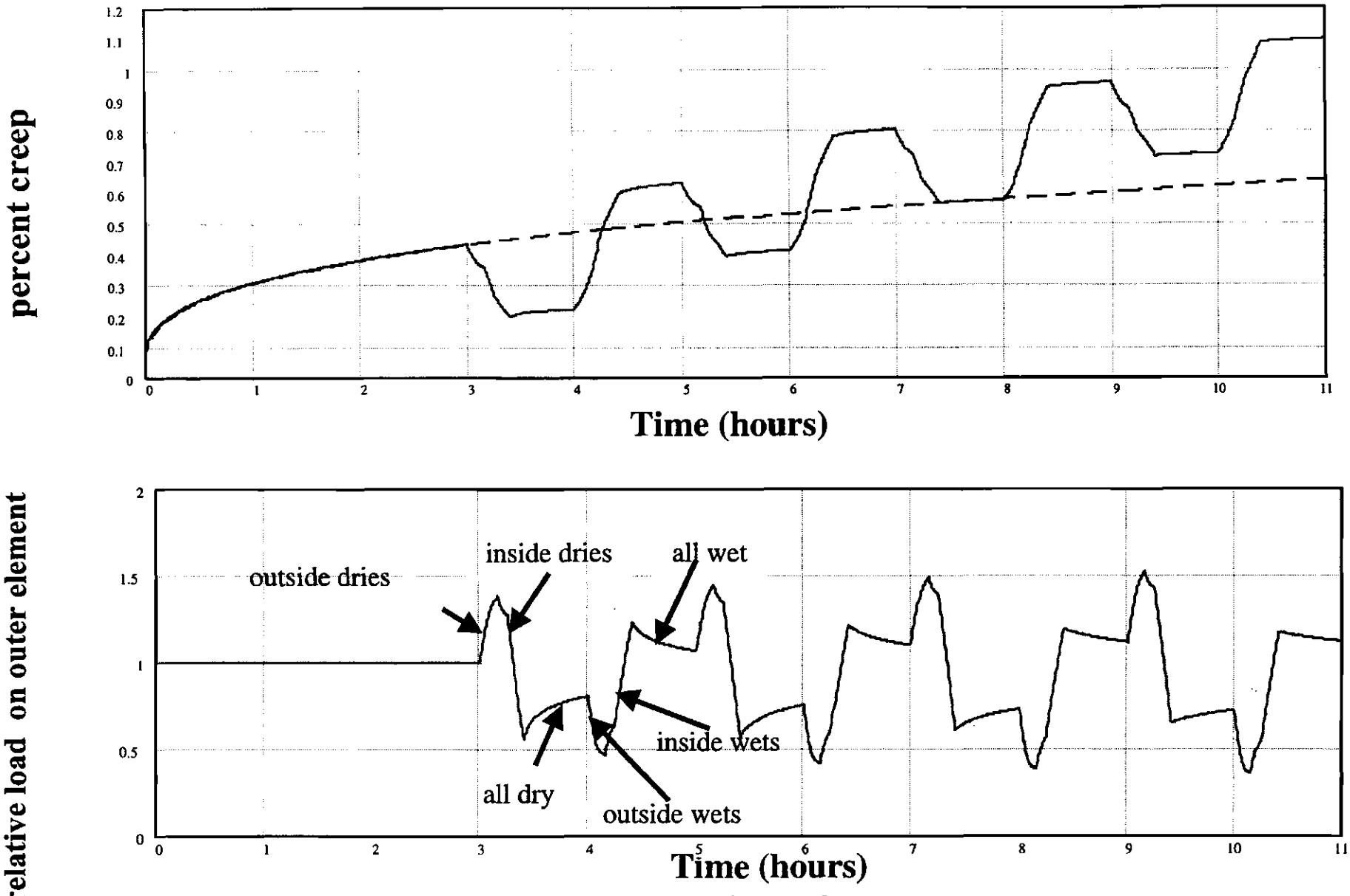

Figure 2

Cyclic humidity creep with 20-minute sorption time

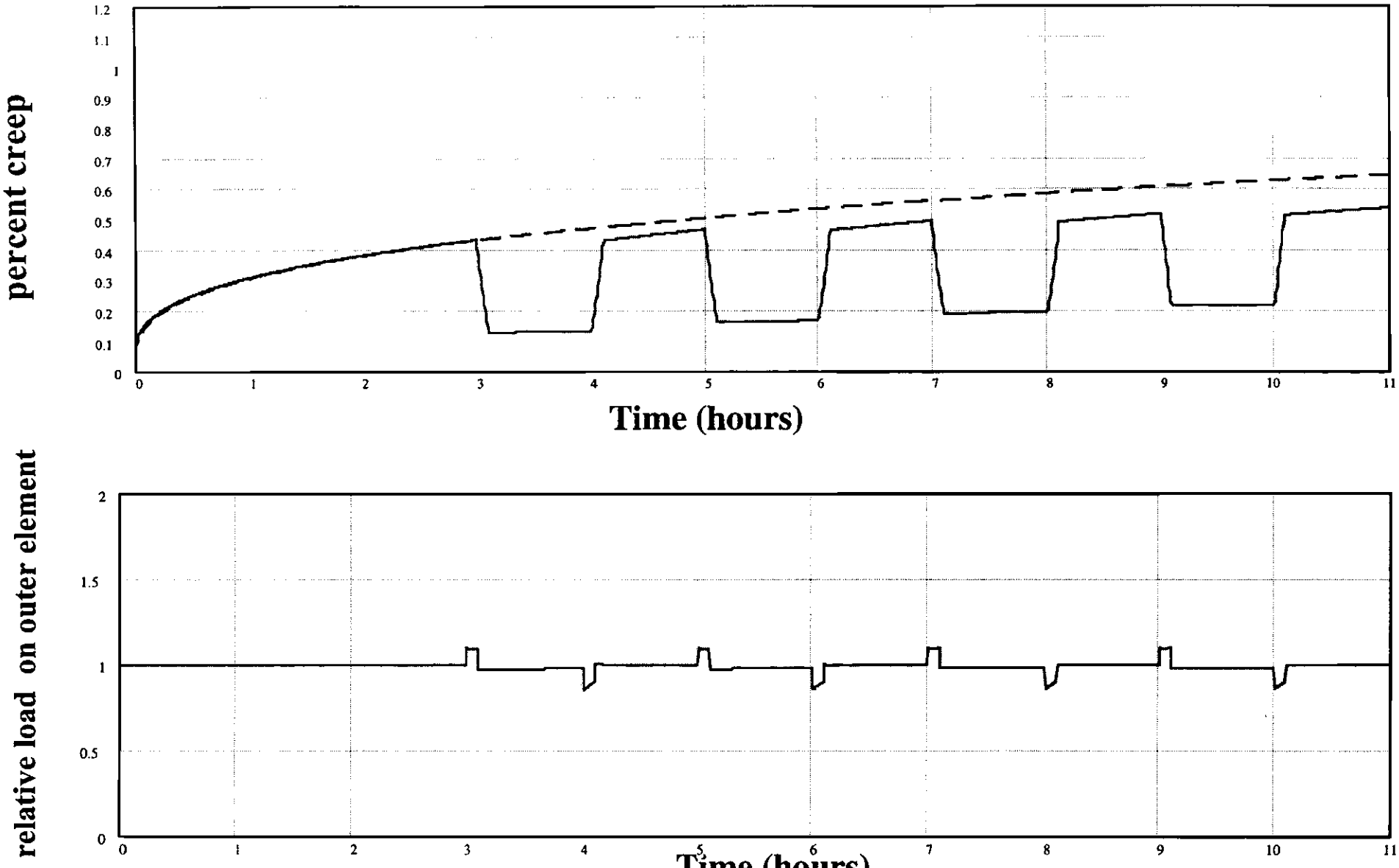

Figure 3

Cyclic humidity creep with 2-minute sorption time

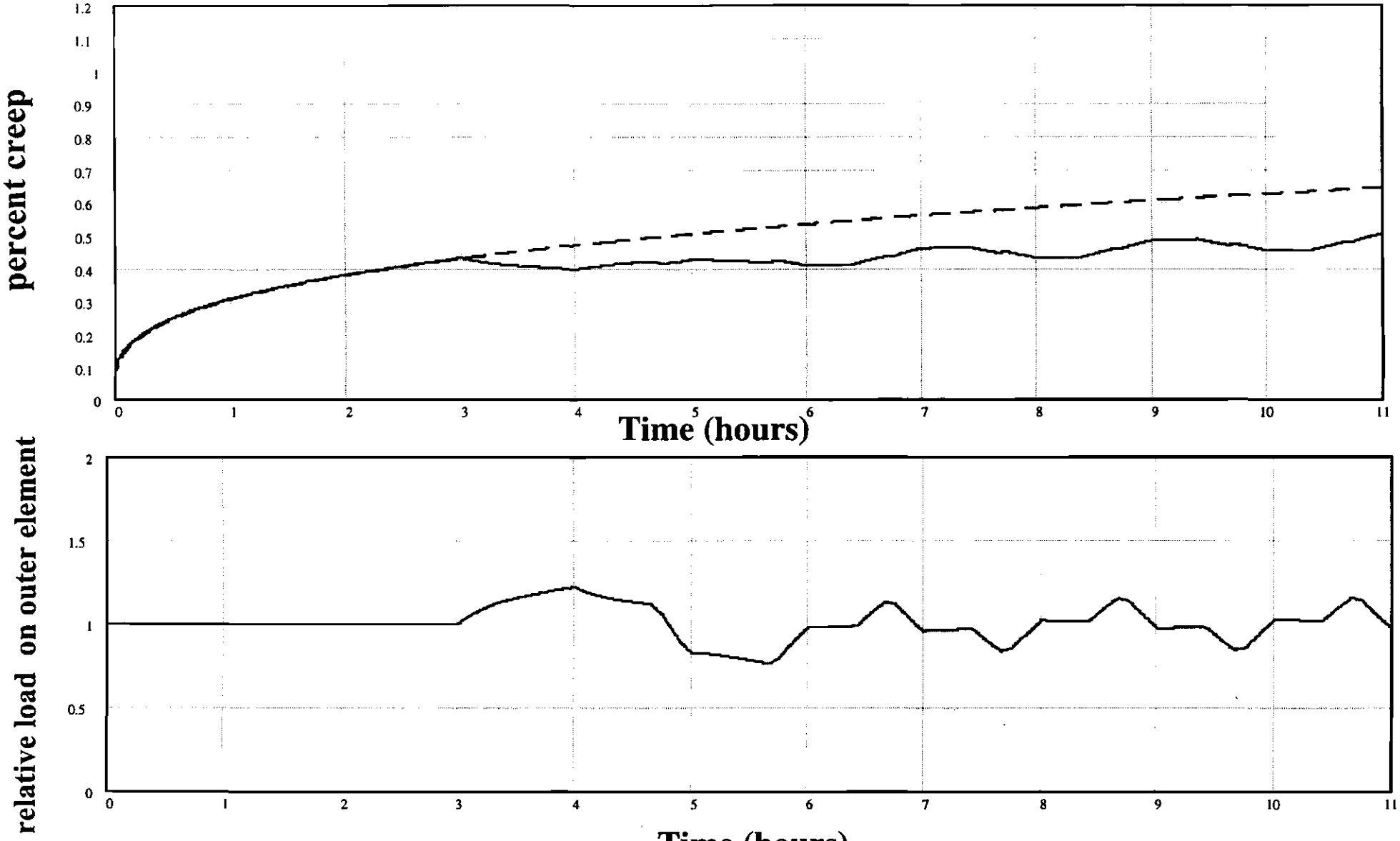

Figure 4

Cyclic humidity creep with 200-minute sorption time

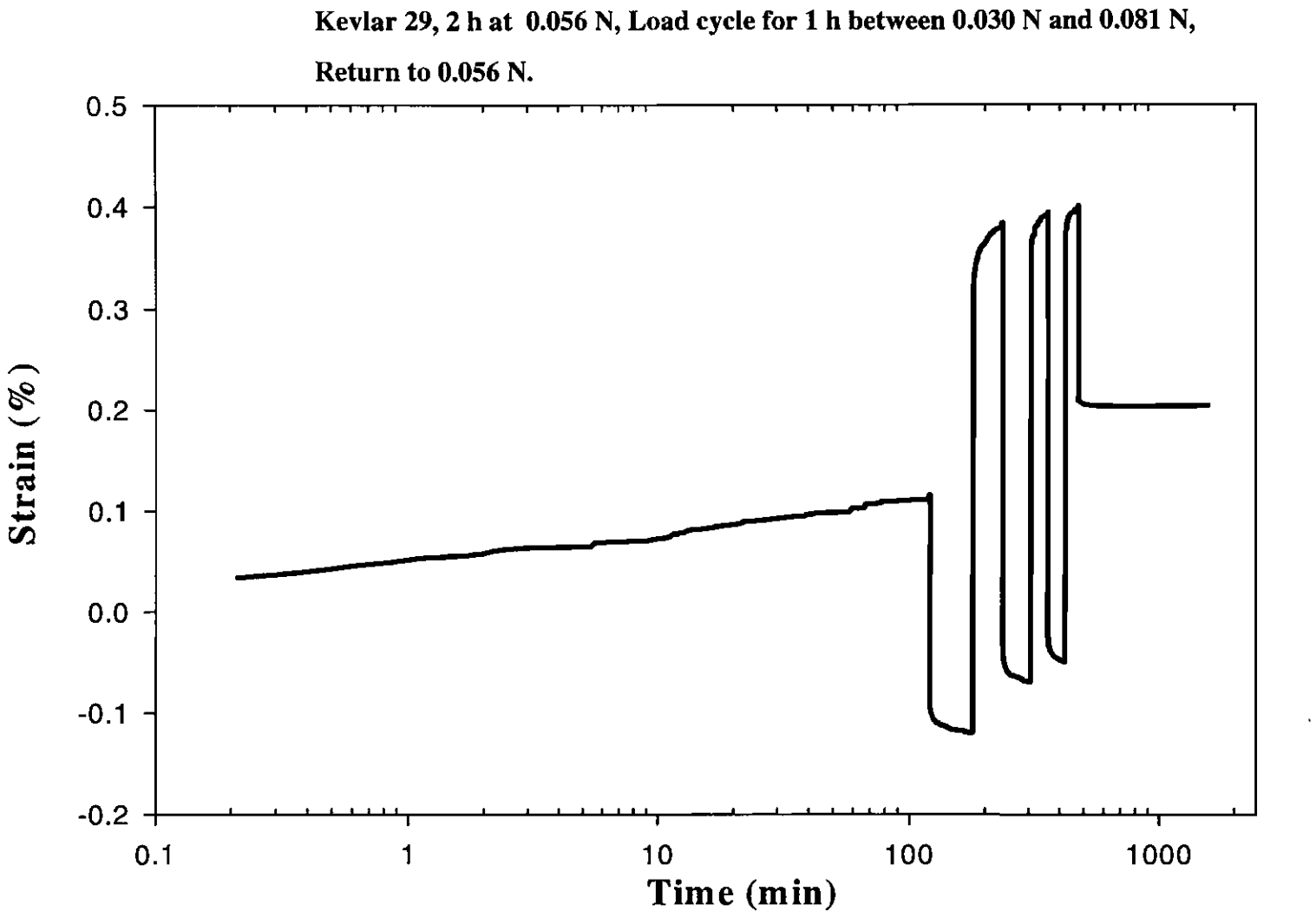

Figure 5
Experimental results of cyclic-load creep for a 1.5-denier Kevlar 29 fiber (RH:90%).

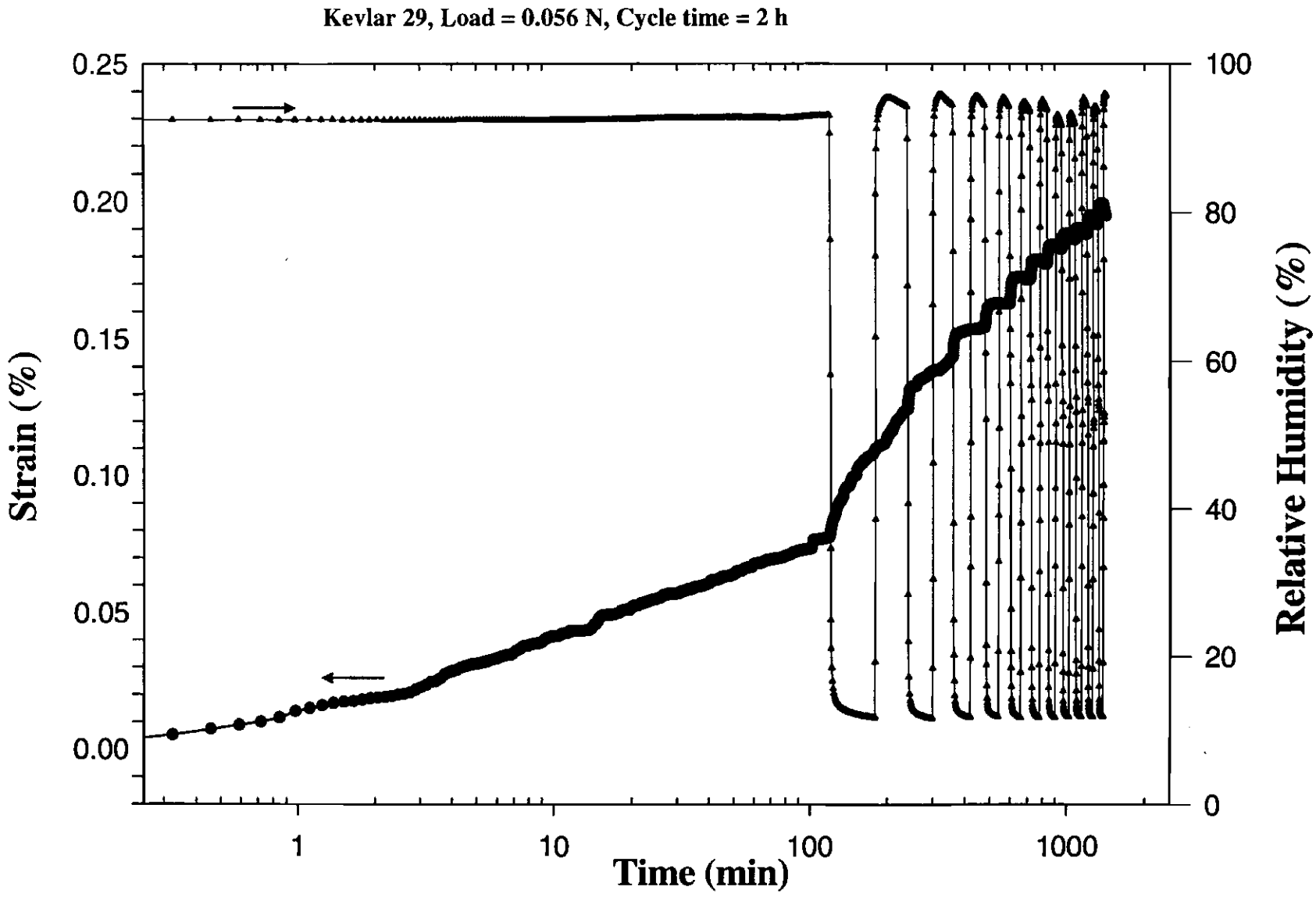

Figure 6
Accelerated creep for a 1.5-denier Kevlar 29 fiber under a 0.056-N load (RH:90-10%).

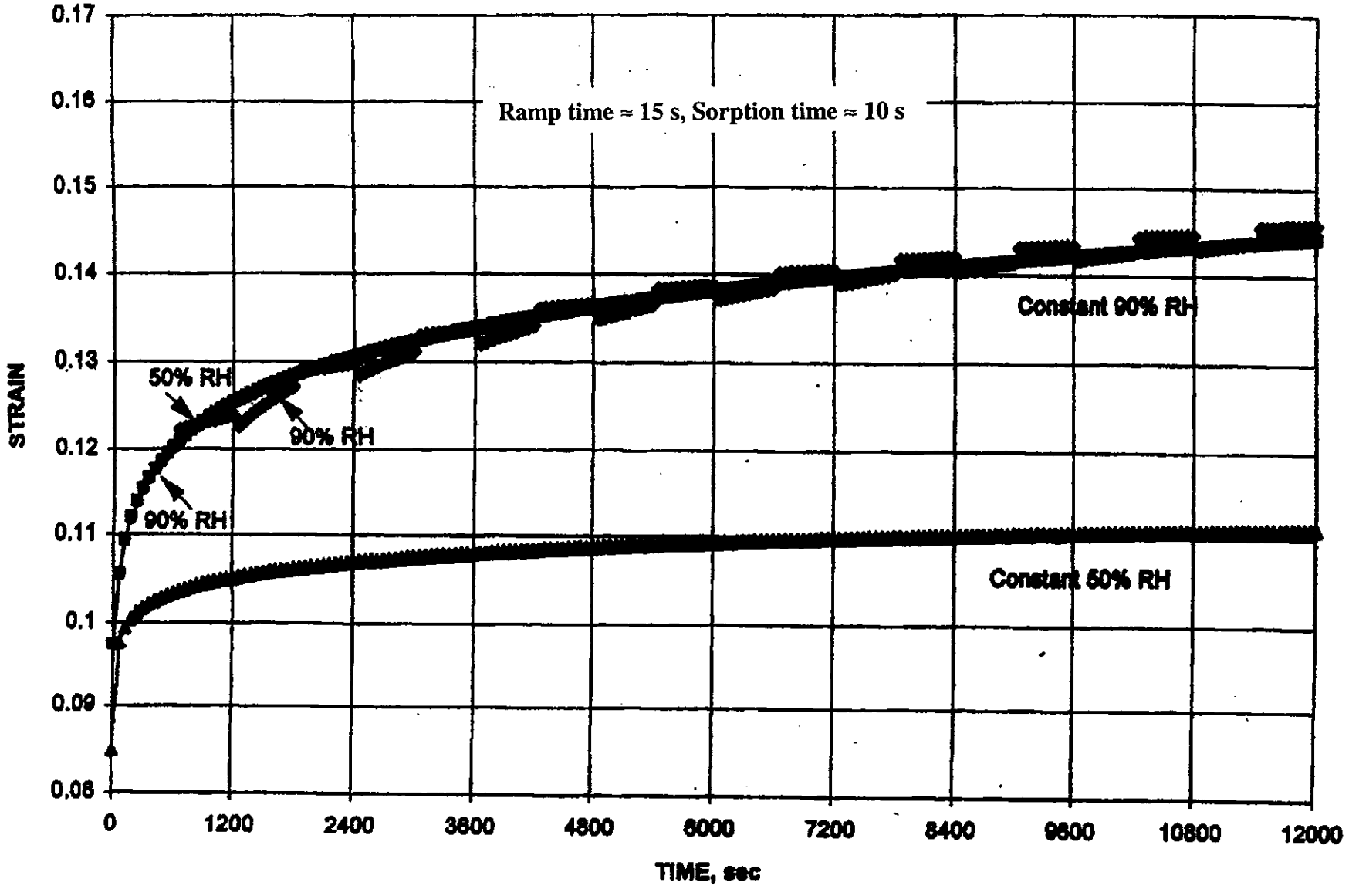

Figure 7
Experimental results of cyclic humidity creep for a single wood fiber (Sedlachek, 1995).

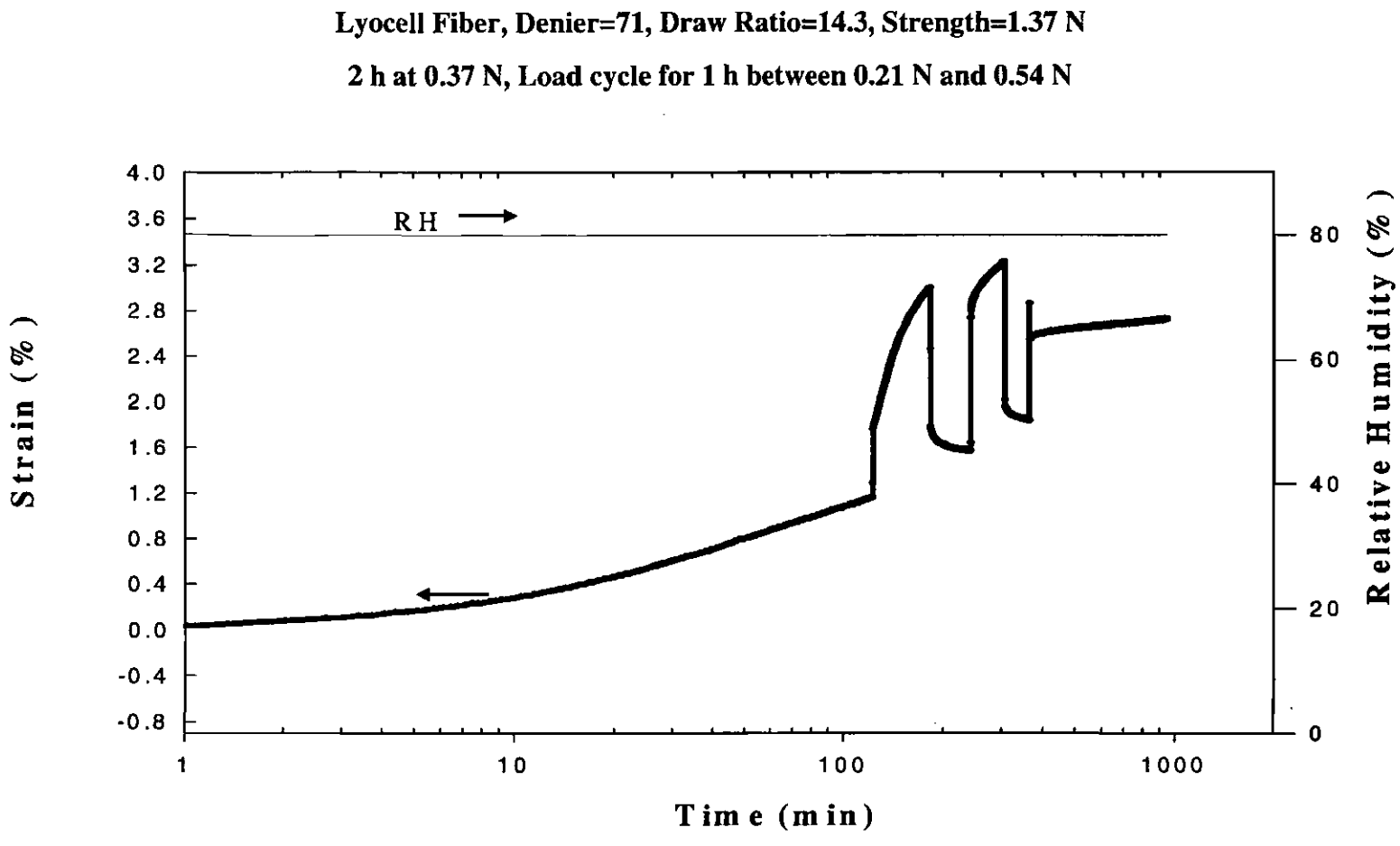

Figure 8

Experimental results of cyclic- load creep for a 71-denier lyocell fiber (RH:90%).

Lyocell Fiber, Denier=11, Draw Ratio= 5.8, Strength=0.44 N

Load = 0.16 N, Full Cycle Times = 10, 30, 120, 360 minutes.

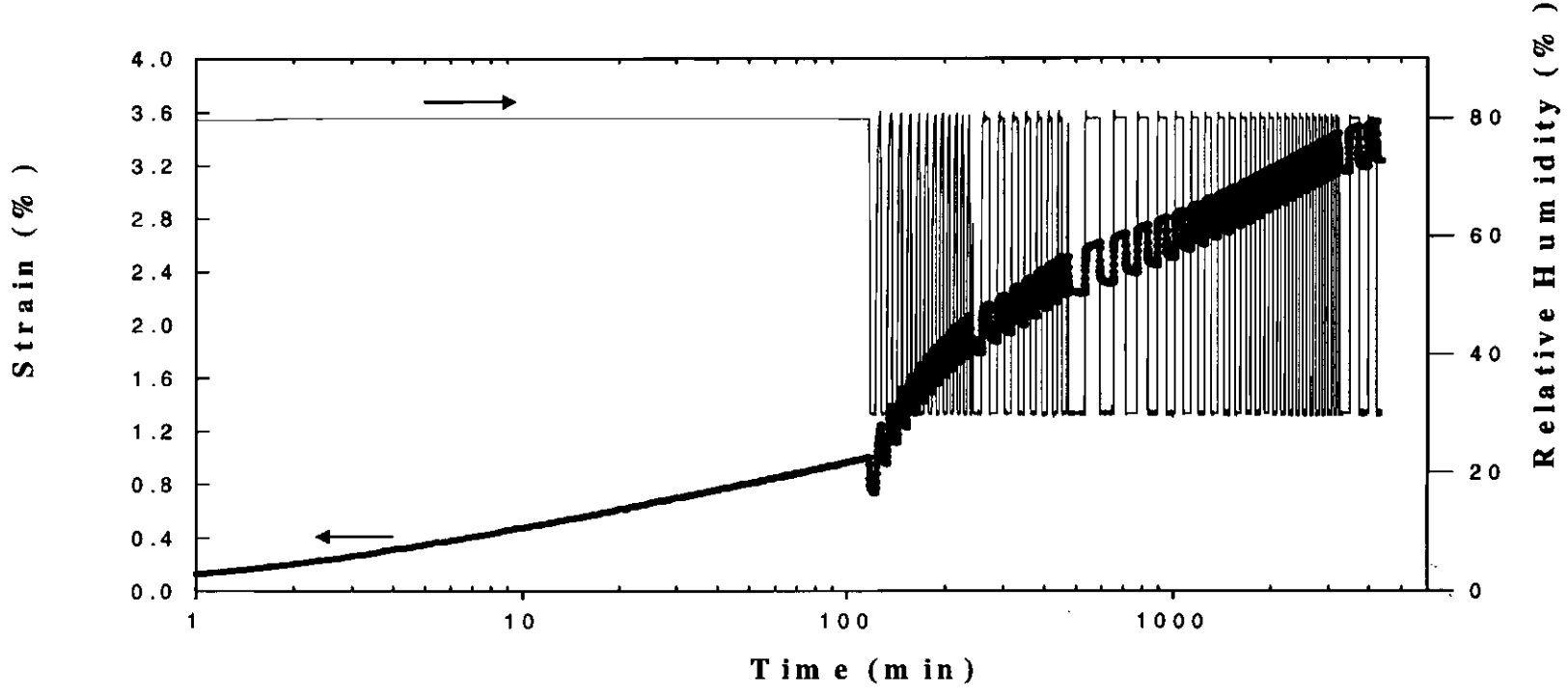

Figure 9

Accelerated creep for an 11-denier lyocell fiber under a 0.16-N load.

Lyocell Fiber, Denier=177, Draw Ratio= 5.7, Strength=5.64 N

Load = 2.0 N, Full Cycle Times = 10, 30, 120, 360 minutes.

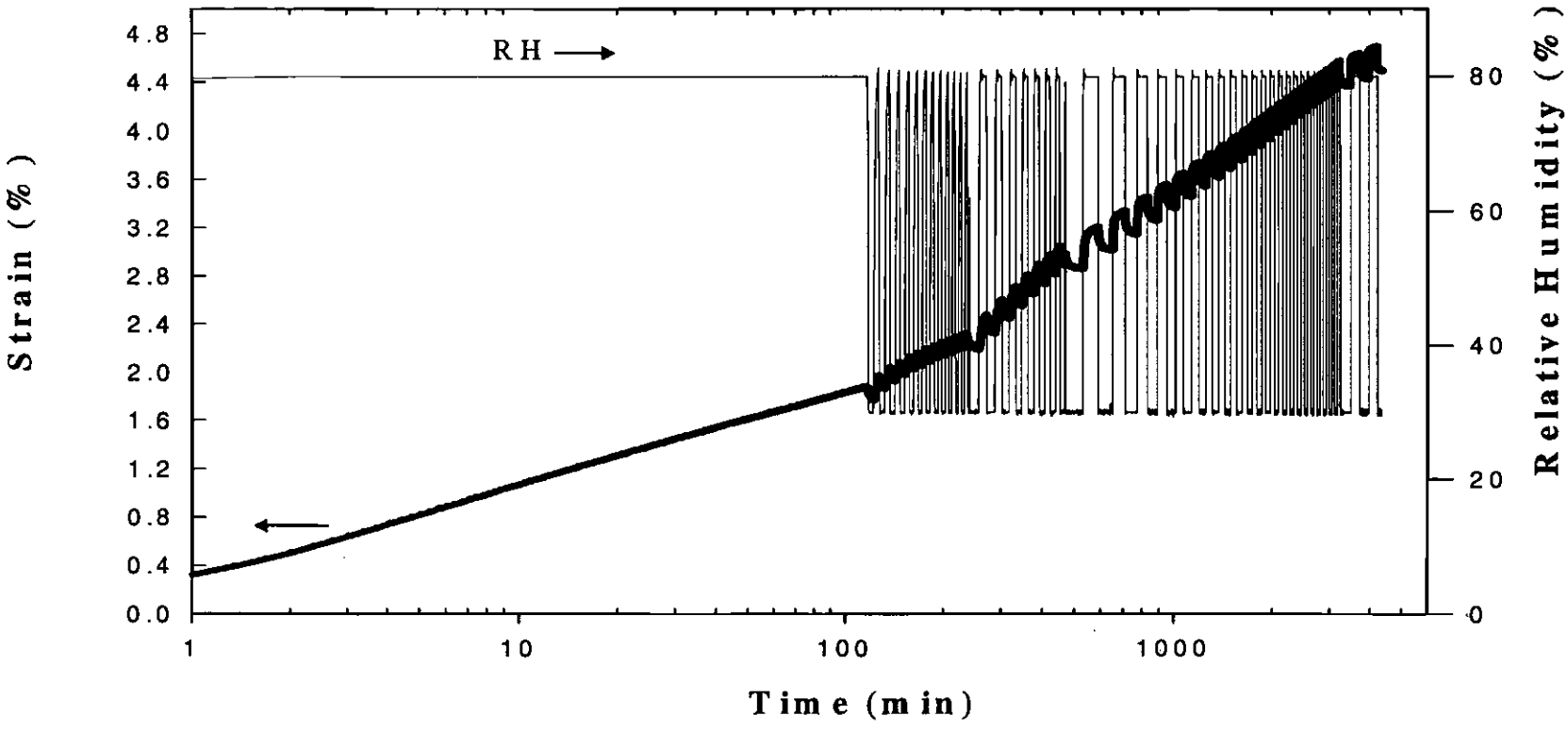

Figure 10

Accelerated creep for a 177-denier lyocell fiber under a 2.0-N load.

Ramie Fiber, Diameter=30 μm, Strength = 0.24 N

Load = 0.1 N, Full Cycle Times = 10, 30, 120, 360 minutes.

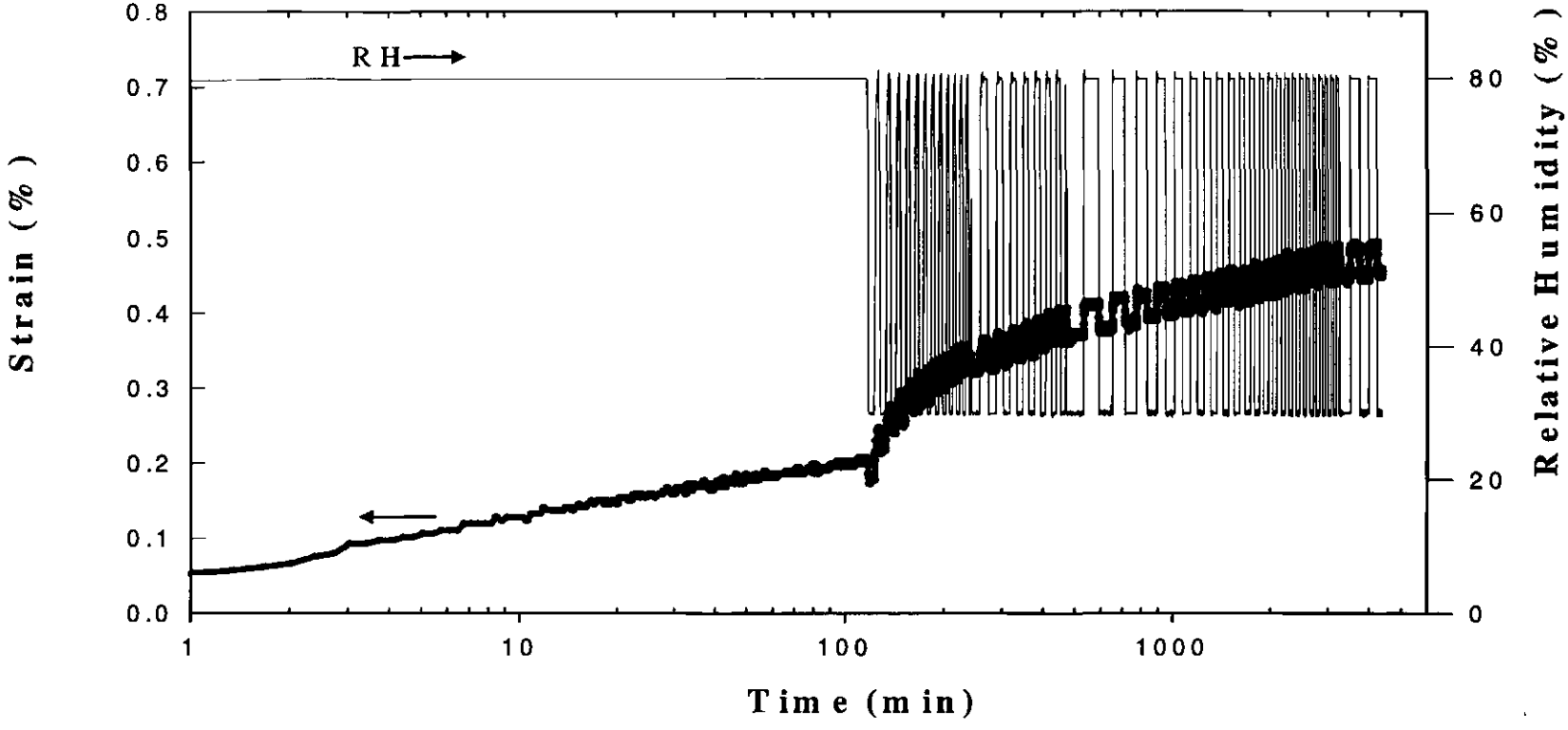

Figure 11

Accelerated creep for 30-μm ramie fiber under a 0.1-N load.

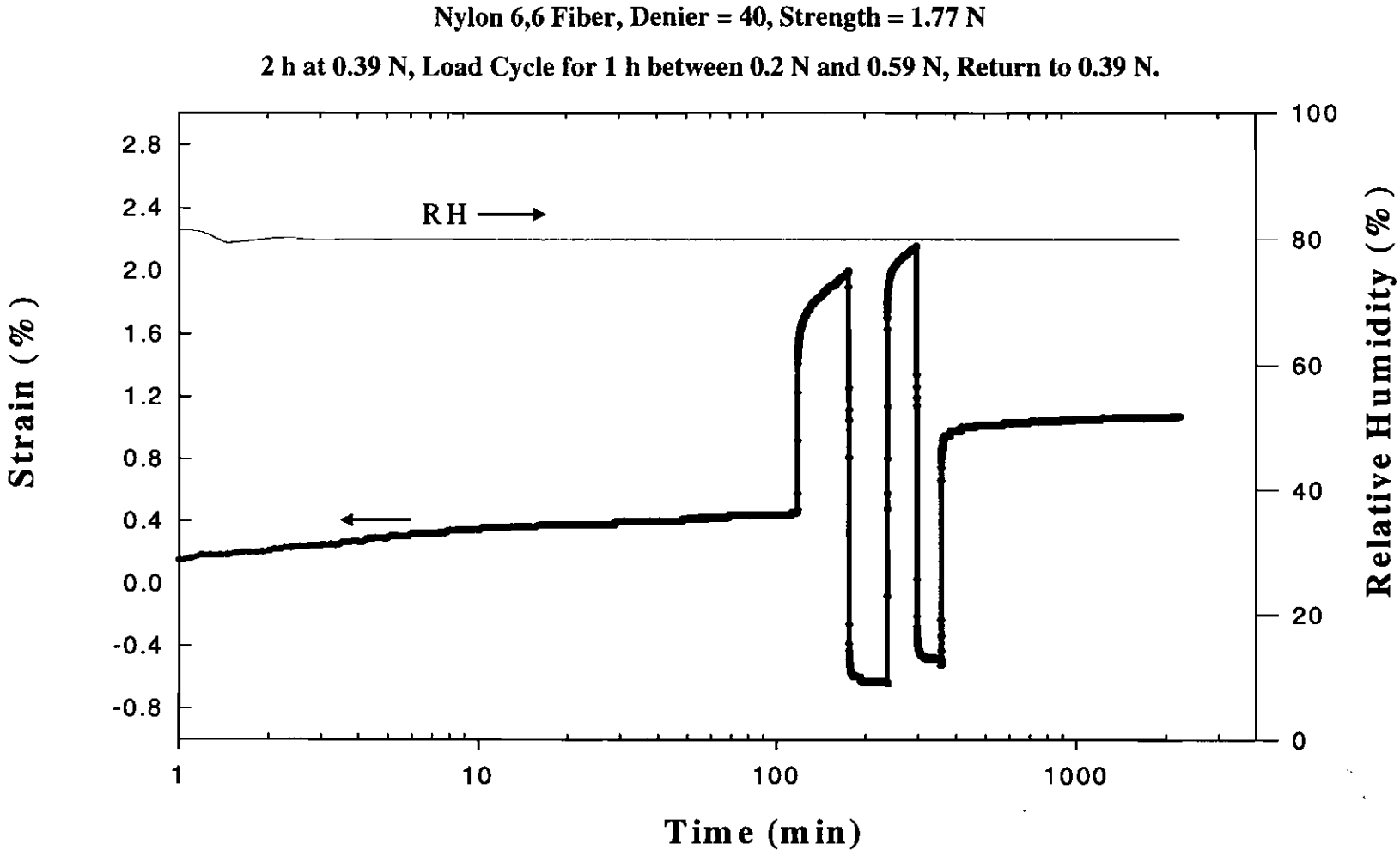

Figure 12
Experimental results of cyclic-load creep for a Nylon 6,6 fiber (RH: 80%).

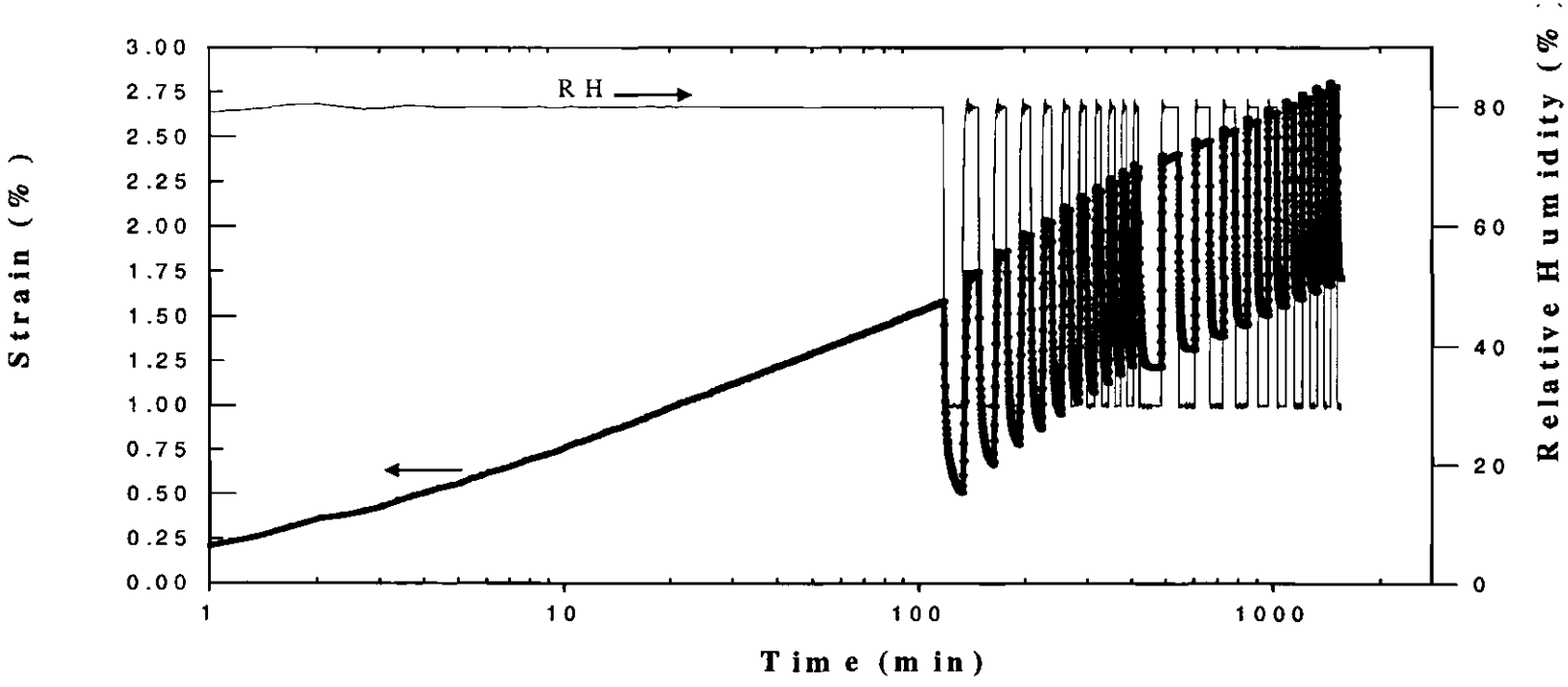

Figure 13

Accelerated creep for a 15-denier Nylon 6,6 fiber under a 0.15-N load.

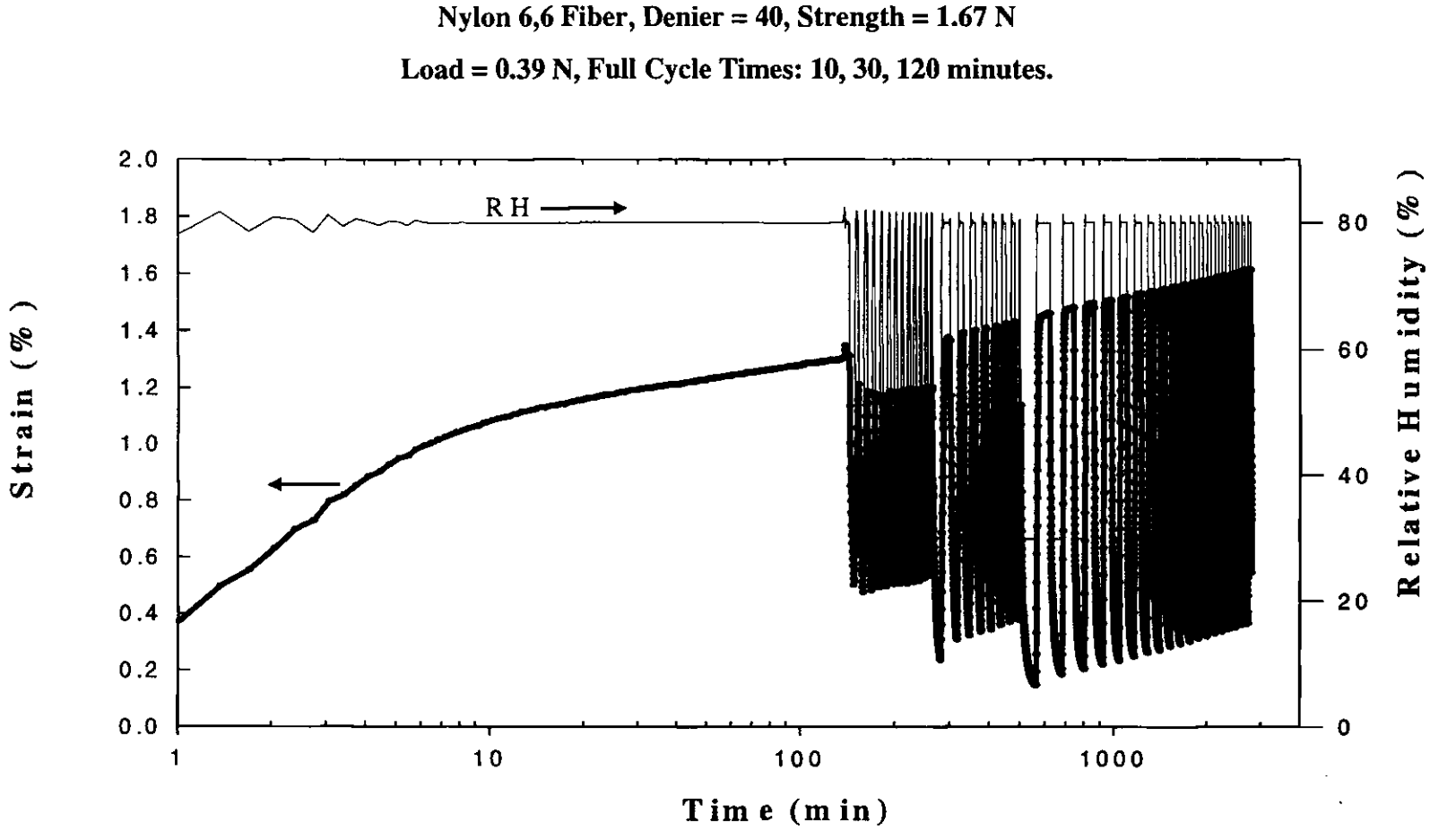

Figure 14

Accelerated creep for a 40-denier Nylon 6,6 fiber under a 0.39-N load.